Light-driven Molecular Rotor: Unidirectional Rotation Controlled by a Single Stereogenic Center

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Supporting Information

trans- and *cis*-2-methoxy-9-(2',3'-dihydro-2'-methyl-1'*H*-naphtho[2,1-*b*]thiopyran-1'-ylidene)-9*H*-thioxanthene *trans*-1 and *cis*-2

A solution of 2,3-dihydro-2-methyl-1*H*-naphtho[2,1-*b*]thiopyran-1-one hydrazone (222 mg, 0.92 mmol) in dry CH_2Cl_2 (10 mL) was cooled to 0°C, whereupon $MgSO_4$ (approximately 300 mg), Ag_2O (400 mg, 1.73 mmol) and a saturated KOH in methanol (0.5 mL) were added subsequently. The mixture was stirred at 0°C for 5 min when the color of turned deep red. The deep red suspension was stirred at 0°C for 30 min and filtered into another bulb. The remaining residue was washed with cold CH_2Cl_2. To the deep red clear solution was added a solution of 2-methoxy-9*H*-thioxanthene-9-thione (238 mg, 0.92 mmol) in CH_2Cl_2 (15 mL). Evolution of nitrogen was observed and the deep red color slowly disappeared. The reaction mixture was stirred overnight at room temperature. After evaporation of the solvents under reduced pressure, the unreacted thioketone was removed by column chromatography (silica gel; hexane:toluene = 10:1). The crude mixture was further purified by column chromatography (silica gel; hexane:EtOAc = 50:1) to obtain *trans*- and *cis*-episulfide (259 mg, 0.55 mmol, 60%), however, it was impossible to separate *cis*- and *trans*-episulfide.

cis-episulfide (259 mg, 0.55 mmol, 60%), however, it was impossible to separate *cis*- and *trans*-episulfide.

To a stirred solution of a mixture of *trans*- and *cis*-episulfide in *p*-xylene (15 mL) was added Cu-bronze powder (350 mg, 5.5 mmol). After refluxed overnight the mixture was allowed to cool down to room temperature. The brown copper residue was removed by silica gel filtration and washed with CH_2Cl_2, and the solvents removed under reduced pressure to obtain a mixture of *trans*-olefin **1** and *cis*-olefin **2**. *Trans*- and *cis*-olefin were separated by HPLC on silica gel (hexane:EtOAc = 50:1) to obtain pure *trans*-olefin **1** (115 mg, 0.26 mmol, 47%); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.57 (1H, d, J = 8.4 Hz), 7.55-7.48 (3H, m), 7.35 (1H, d, J = 8.4 Hz), 7.25 (1H, d, J = 6.6 Hz), 7.15 (1H, d, J = 2.6 Hz), 7.09 (1H, ddd, J = 8.1, 6.6, 1.4 Hz), 6.97 (1H, ddd, J = 8.1, 7.1, 1.1 Hz), 6.84 (1H, dd, J = 8.8, 2.6 Hz), 6.73-6.67 (1H, m), 6.41-6.34 (2H, m), 4.17 (1H, ddq, J = 7.3, 2.9, 7.0 Hz), 3.86 (3H, s), 3.69 (1H, dd, J = 11.4, 7.3 Hz), 3.08 (1H, dd, J = 11.4, 2.9 Hz), 0.78 (3H, d, J = 7.0 Hz) ; ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.3, 138.3, 137.6, 136.5, 134.89, 134.85, 132.7, 131.4, 131.3, 130.7, 128.9, 128.6, 127.50, 127.45, 127.3, 126.4, 126.0, 125.8, 125.4, 125.2, 124.4, 124.3, 113.8, 112.2, 55.6, 37.1, 32.3, 19.2; HRMS Calcd for $C_{28}H_{22}OS_2$: 438.11120. Found: 438.10954, and pure *cis*-olefin **2** (107 mg, 0.24 mmol, 44%); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.62-7.52 (5H, m), 7.37 (1H, d, J = 8.8 Hz), 7.33, (1H, dt, J = 1.5, 7.7 Hz), 7.25 (1H, dt, J = 1.5, 7.7 Hz), 7.12 (1H, d, J = 8.8 Hz), 7.11 (1H, br t, J = 7.0 Hz), 7.00 (1H, br t, J = 7.0 Hz), 6.30 (1H, dd, J = 8.4, 2.6 Hz), 5.92 (1H, d, J = 2.6 Hz), 4.11 (1H, ddq, J = 7.3, 3.3, 7.0 Hz), 3.69 (1H, dd, J = 11.5, 7.3 Hz), 3.06 (1H, dd, J = 11.5, 3.3 Hz), 3.01 (3H, s), 0.79 (3H, d, J = 7.0 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 157.6, 139.4, 136.7, 136.5, 135.9, 134.8, 132.6, 131.5, 131.4, 130.9, 127.7, 127.5, 127.45, 127.38, 127.2, 126.7, 126.0, 125.9, 125.43, 125.36, 124.5, 124.3, 114.4, 112.9, 54.8, 37.2, 32.3, 19.2; HRMS Calcd for $C_{28}H_{22}OS_2$: 438.11120. Found: 438.10986.

Enantioresolution of *trans*-olefin **1** was accomplished by preparative chiral HPLC (Chiralpak OD, heptane:isopropanol = 99:1). The second fraction was crystallized from *n*-hexane to obtain colorless prisms: mp 214.9°C, suitable for X-ray crystallographic analysis. A single crystal (dimensions of 0.25 x 0.33 x 0.38 mm) was selected for data collection and mounted on an Enraf-Nonius *CAD*-4*F*[1] diffractometer, interfaced to a *Debian-Linux* computer (Mo tube, 50 kV, 40 mA, monochromated Mo-K radiation (0.71073Å), $\Delta\omega = 0.85 + 0.34$ tg θ). Unit cell parameters and orientation matrix were determined from a least-squares treatment of the *SET4* setting angles of 22 reflections in the range $16.57° < \theta < 20.28°$. The crystal data of (2'*R*)-(*M*)-*trans*-olefin **1**: $C_{28}H_{22}OS_2$, *M*r = 438.61; orthorhombic; space group $P2_12_12_1$; $a = 10.201(1)$, $b = 12.274(1)$, $c = 17.431(1)$Å; $V = 2182.5(3)$Å^3; $Z = 4$; $Dx = 1.335$ g cm^{-3}. The intensities of three standard reflections, monitored every three hours of X-ray exposure time, showed no greater fluctuations during data collection than those expected from Poisson statistics. The structure was solved by Patterson methods and extension of the model was accomplished by direct methods applied to difference structure factors using the program *DIRDIF*. The positional and anisotropic displacement parameters for the non-hydrogen atoms were refined. A subsequent difference Fourier synthesis resulted in the location of all hydrogen atoms, which coordinates and isotropic displacement parameters were refined. Final refinement on F^2 carried out by full-matrix least-squares techniques converged at $wR(F^2)$ = 0.0992 for 4735 reflections and $R(F)$ = 0.0381 for 4150 reflections with $F_0 \geq 4.0\ \sigma(F_0)$ and 367 parameters. The final difference Fourier map was essential featureless: no significant peaks (0.22(4) e/Å^3) having chemical meaning above the general background were observed. The absolute structure actually chosen was determined by Flack's x-refinement (x = –0.07(7)). The UV spectrum of *trans*-olefin **1** shows intense absorption band: UV (hexane) λ_{max} 325 nm (ε 8300), 259 (35100), 222 (51300). The CD spectrum of (2'*R*)-(*M*)-*trans*-olefin

1, which was collected as the second fraction of enantioresolution by chiral HPLC, exhibits very intense Cotton effect: CD (hexane) λ_{ext} 349.8 nm ($\Delta\varepsilon$ +19.1), 318.6 (+15.4), 277.2 (–155.4), 253.0 (+40.8), 223.8 (+98.1).

Enantioresolution of *cis*-olefin **2** was achieved by preparative chiral HPLC (Chiralpak OD, heptane:isopropanol = 99:1). The UV spectrum of *cis*-olefin **2** shows intense absorption band: UV (hexane) λ_{max} 321 nm (ε 7400), 266 (28200), 248 (29100), 213 (50500). The CD spectrum of (2'*S*)-(*P*)-*cis*-olefin **2** exhibits very intense Cotton effect: CD (hexane) λ_{ext} 356.8 nm ($\Delta\varepsilon$ –14.7), 325.4 (+2.7), 276.4 (+120.6), 252.2 (–76.1), 223.2 (–92.4).

9-(2',3'-dihydro-2'-methyl-1'*H*-naphtho[2,1-*b*]thiopyran-1'-ylidene)-9*H*-thioxanthene 5

A solution of 2,3-dihydro-2-methyl-1*H*-naphtho[2,1-*b*]thiopyran-1-one hydrazone (210 mg, 0.87 mmol) in dry CH_2Cl_2 (10 mL) was cooled to 0°C, whereupon $MgSO_4$ (approximately 300 mg), Ag_2O (400 mg, 1.73 mmol) and a saturated KOH in methanol (0.5 mL) were added subsequently. The mixture was stirred at 0°C for 5 min when the color of turned deep red. The deep red suspension was stirred at 0°C for 30 min and filtered into another bulb. The remaining residue was washed with cold CH_2Cl_2. To the deep red clear solution was added a solution of 9*H*-thioxanthene-9-thione (198 mg, 0.87 mmol) in CH_2Cl_2 (15 mL). Evolution of nitrogen was observed and the deep red color slowly disappeared. The reaction mixture was stirred overnight at room temperature. After evaporation of the solvents under reduced pressure, the unreacted thioketone was removed by column chromatography (silica gel; hexane:toluene = 10:1). The crude mixture was further purified by column chromatography (silica gel; hexane:EtOAc = 50:1). After crystallization from *n*-hexane, episulfide was obtained as colorless crystals (230 mg, 0.52 mmol, 60%): mp 200.4-200.5°C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.88 (1H, br d, J = 8.8 Hz), 8.03-7.99 (1H, m), 7.56 (1H, br d,

J = 8.1 Hz), 7.48 (1H, ddd, J = 8.8, 7.0, 1.5 Hz), 7.45-7.41 (1H, m), 7.33 (1H, ddd, J = 8.1, 6.6, 1.1 Hz), 7.31-7.26 (4H, m), 7.03 (1H, dd, J = 7.7, 1.1 Hz), 6.95 (1H, d, J = 8.4 Hz), 6.82 (1H, dd, J = 8.1, 1.5 Hz), 6.72 (1H, dt, J = 1.5, 7.7 Hz), 6.24 (1H, ddd, J = 8.1, 7.0, 1.1 Hz), 2.64 (1H, dd, J = 12.1, 7.7 Hz), 2.52 (1H, ddq, J = 7.7, 5.5, 7.0 Hz), 2.23 (1H, dd, J = 12.1, 5.5 Hz), 1.19 (3H, d, J = 7.0 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 139.1, 136.4, 134.7, 133.7, 132.0, 131.5, 131.23, 131.20, 129.6, 128.1, 127.4, 126.9, 126.5, 126.31, 126.29, 125.6, 125.4, 125.2, 125.0, 124.5, 124.0, 123.3, 65.0, 62.0, 40.2, 34.5, 20.5; HRMS Calcd for $C_{27}H_{20}S_3$: 440.07271. Found: 440.07264. To a stirred solution of episulfide (120 mg, 0.27 mmol) in *p*-xylene (20 mL) was added Cu-bronze powder (172 mg, 2.7 mmol). After refluxed overnight the mixture was allowed to cool down to room temperature. The brown copper residue was removed by silica gel filtration and washed with CH_2Cl_2, and the solvents removed under reduced pressure. The crude product was purified by recrystallization from *n*-hexane to obtain olefin **5** as colorless prisms (106 mg, 0.26 mmol, 95%): mp 220.4-220.6°C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.64-7.58 (3H, m), 7.56-7.54 (2H, m), 7.38 (1H, d, J = 8.4 Hz), 7.36 (1H, dt, J = 1.1, 7.3 Hz), 7.30-7.26 (2H, m), 7.11 (1H, ddd, J = 8.1, 7.0, 1.1 Hz), 6.99 (1H, ddd, J = 8.4, 7.0, 1.5 Hz), 6.73 (1H, ddd, J = 7.7, 6.6, 2.2), 6.43-6.38 (2H, m), 4.13 (1H, ddq, J = 7.3, 2.9, 6.6 Hz), 3.72 (1H, dd, J = 11.4, 7.3 Hz), 3.09 (1H, dd, J = 11.4, 2.9 Hz), 0.78 (3H, d, J = 6.6 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.2, 136.4, 136.1, 136.0, 134.9, 134.2, 132.4, 131.3, 131.2, 130.7, 129.0, 127.7, 127.6, 127.5, 126.7, 126.4, 126.1, 126.0, 125.7, 125.4, 125.3, 124.34, 124.30, 37.2, 32.1, 19.2; HRMS Calcd for $C_{27}H_{20}S_2$: 408.10064. Found: 408.10164.

2,7-dimethoxy-9-(2',3'-dihydro-2'-methyl-1'*H*-naphtho[2,1-*b*]thiopyran-1'-ylidene)-9*H*-thioxanthene 7

A solution of 2,3-dihydro-2-methyl-1*H*-naphtho[2,1-*b*]thiopyran-1-one hydrazone (145 mg, 0.60 mmol) in dry CH_2Cl_2 (10 mL) was cooled to 0°C, whereupon $MgSO_4$ (approximately 300 mg), Ag_2O (400 mg, 1.73 mmol) and a saturated KOH in methanol (0.5 mL) were added subsequently. The mixture was stirred at 0°C for 5 min when the color of turned deep red. The deep red suspension was stirred at 0°C for 30 min and filtered into another bulb. The remaining residue was washed with cold CH_2Cl_2. To the deep red clear solution was added a solution of 2,7-dimethoxy-9*H*-thioxanthene-9-thione (120 mg, 0.42 mmol) in CH_2Cl_2 (15 mL). Evolution of nitrogen was observed and the deep red color slowly disappeared. The reaction mixture was stirred overnight at room temperature. After evaporation of the solvents under reduced pressure, the crude product was purified by column chromatography (silica gel; hexane:EtOAc = 20:1) and further purified by HPLC on silica gel (hexane:EtOAc = 50:1) to obtain episulfide (220 mg, 0.44 mmol, 73%) as colorless solids; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.84 (1H, br d, J = 8.8 Hz), 7.62 (1H, d, J = 2.9 Hz), 7.59 (1H, d, J = 8.8 Hz), 7.34-7.28 (3H, m), 6.96 (1H, d, J = 8.4 Hz), 6.89 (1H, d, J = 8.4 Hz), 6.87 (1H, dd, J = 8.4, 2.9 Hz), 6.40 (1H, d, J = 2.6 Hz), 6.31 (1H, d, J = 8.4, 2.6 Hz), 3.86 (3H, s), 2.79 (3H, s), 2.70 (1H, dd, J = 11.7, 8.1 Hz), 2.60 (1H, ddq, J = 8.1, 5.1, 6.6 Hz), 2.23 (1H, dd, J = 11.7, 5.1 Hz), 1.18 (3H, d, J = 6.6 Hz) ; ^{13}C NMR (75 MHz, $CDCl_3$) δ 157.8, 156.8, 139.4, 134.7, 132.4, 132.3, 132.0, 128.4, 128.0, 127.4, 127.0, 126.5, 126.4, 125.7, 125.3, 125.1, 124.0, 123.3, 117.5, 115.1, 113.5, 113.1, 65.0, 62.7, 55.5, 54.1, 40.2, 34.8, 20.5; HRMS Calcd for $C_{29}H_{24}O_2S_3$: 500.09383. Found: 500.09362. To a stirred solution of episulfide (200 mg, 0.40 mmol) in *p*-xylene (20 mL) was added Cu-bronze powder (255 mg, 4.0 mmol). After refluxed overnight the mixture was allowed to cool down to room temperature. The brown copper residue was removed by silica gel filtration and washed with CH_2Cl_2, and the solvents removed under reduced pressure. The crude product was purified by recrystallization from *n*-

hexane to obtain olefin **7** as colorless prisms (185 mg, 0.40 mmol, 99%): mp 149.0-149.2°C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.60 (1H, d, J = 8.8 Hz), 7.56 (1H, br d, J = 7.3 Hz), 7.51 (1H, d, J = 8.8 Hz), 7.38 (1H, d, J = 8.4 Hz), 7.17 (1H, d, J = 2.6 Hz), 7.14 (1H, m), 7.12 (1H, d, J = 8.8 Hz), 7.01 (1H, br t, J = 7.7 Hz), 6.85 (1H, dd, J = 8.8, 2.9 Hz), 6.30 (1H, dd, J = 8.4, 2.6 Hz), 5.93 (1H, d, J = 2.9 Hz), 4.20 (1H, ddq, J = 7.7, 3.3, 6.6 Hz), 3.88 (3H, s), 3.71 (1H, dd, J = 11.4, 7.7 Hz), 3.08 (1H, dd, J = 11.4, 3.3 Hz), 3.03 (3H, s), 0.82 (3H, d, J = 6.6 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.3, 157.6, 139.4, 137.4, 136.6, 134.9, 132.8, 131.54, 131.46, 130.9, 128.6, 127.9, 127.47, 127.43, 127.2, 126.1, 126.0, 125.4, 124.5, 124.4, 114.4, 113.9, 112.9, 112.2, 55.6, 54.9, 37.2, 32.4, 19.3; HRMS Calcd for $C_{29}H_{24}O_2S_2$: 468.12176. Found: 468.12165.

9-(2',3'-dihydro-2'-methyl-1'*H*-naphtho[2,1-*b*]thiopyran-1'-ylidene)-9*H*-xanthene 9

A solution of 2,3-dihydro-2-methyl-1*H*-naphtho[2,1-*b*]thiopyran-1-one hydrazone (210 mg, 0.87 mmol) in dry CH_2Cl_2 (10 mL) was cooled to 0°C, whereupon $MgSO_4$ (approximately 300 mg), Ag_2O (400 mg, 1.73 mmol) and a saturated KOH in methanol (0.5 mL) were added subsequently. The mixture was stirred at 0°C for 5 min when the color of turned deep red. The deep red suspension was stirred at 0°C for 30 min and filtered into another bulb. The remaining residue was washed with cold CH_2Cl_2. To the deep red clear solution was added a solution of 9*H*-xanthene-9-thione (184 mg, 0.87 mmol) in CH_2Cl_2 (15 mL). Evolution of nitrogen was observed and the deep red color slowly disappeared. The reaction mixture was stirred overnight at room temperature. After evaporation of the solvents under reduced pressure, the crude product was purified by column chromatography (silica gel; hexane:EtOAc = 50:1) and recrystallized from absolute ethanol to obtain episulfide (230 mg, 0.54 mmol, 62%) as colorless prisms: mp 195.7-195.9°C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.69

(1H, br d, J = 8.4 Hz), 7.79 (1H, dd, J = 8.1, 1.5 Hz), 7.72 (1H, br d, J = 8.1 Hz), 7.56 (1H, ddd, J = 8.4, 7.0, 1.5 Hz), 7.43 (1H, ddd, J = 8.1, 7.0, 1.1 Hz), 7.39 (1H, d, J = 8.4 Hz), 7.36 (1H, ddd, J = 8.1, 7.3, 1.5 Hz), 7.20 (1H, dd, J = 8.1, 1.1 Hz), 7.17 (1H, ddd, J = 8.1, 7.3, 1.1 Hz), 6.94 (1H, d, J = 8.4 Hz), 6.93 (1H, br d, J = 8.1 Hz), 6.86 (1H, ddd, J = 8.1, 7.0, 1.5 Hz), 6.16 (1H, dd, J = 8.1, 1.5 Hz), 6.11 (1H, ddd, J = 8.1, 7.0, 1.5 Hz), 3.03 (1H, ddq, J = 9.5, 7.0, 7.0 Hz), 2.46 (1H, dd, J = 12.5, 9.5 Hz), 2.22 (1H, dd, J = 12.5, 7.0 Hz), 1.18 (3H, d, J = 7.0 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 154.6, 153.5, 140.3, 134.5, 132.5, 130.9, 129.6, 128.7, 128.5, 127.6, 127.5, 127.0, 126.2, 125.6, 124.7, 123.0, 122.13, 122.07, 121.4, 120.6, 116.6, 115.4, 64.3, 54.7, 41.7, 36.7, 21.2; HRMS Calcd for $C_{27}H_{20}OS_2$: 424.09555. Found: 424.09294. To a stirred solution of episulfide (70 mg, 0.17 mmol) in *p*-xylene (15 mL) was added Cu-bronze powder (102 mg, 1.6 mmol). After refluxed overnight the mixture was allowed to cool down to room temperature. The brown copper residue was removed by silica gel filtration and washed with CH_2Cl_2, and the solvents removed under reduced pressure. The crude product was purified by recrystallization from EtOAc to obtain olefin **9** as slightly yellow prisms (63 mg, 0.16 mmol, 97%): mp 238.8-239.0°C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.63 (1H, d, J = 8.4 Hz), 7.60 (1H, br d, J = 8.1 Hz), 7.59 (1H, dd, J = 7.7, 1.1 Hz), 7.38 (1H, d, J = 8.4 Hz), 7.37 (1H, ddd, J = 8.4, 7.0, 1.5 Hz), 7.33 (1H, dt, J = 1.5, 7.7 Hz), 7.29 (1H, br d, J = 8.4 Hz), 7.23 (1H, dt, J = 1.5, 7.7 Hz), 7.12 (1H, ddd, J = 8.1, 7.0, 1.1 Hz), 7.06 (1H, d, J = 8.1 Hz), 6.96 (1H, ddd, J = 8.4, 7.0, 1.5), 6.85-6.81 (1H, m), 6.23-6.20 (2H, m), 4.29 (1H, ddq, J = 7.0, 2.6, 6.6 Hz), 3.77 (1H, dd, J = 11.0, 7.0 Hz), 3.21 (1H, dd, J = 11.0, 2.6 Hz), 0.79 (3H, d, J = 6.6 Hz) ^{13}C NMR (125 MHz, $CDCl_3$) δ 154.9, 153.4, 134.8, 134.5, 131.4, 130.8, 130.3, 128.3, 128.2, 127.7, 127.6, 127.5, 126.8, 126.2, 125.8, 125.1, 124.3, 124.0, 123.4, 123.0, 122.2, 116.9, 115.9, 37.0, 30.8, 18.5; HRMS Calcd for $C_{27}H_{20}OS$: 392.12348. Found: 392.12243.

Irradiation Experiments

Irradiation of solution of racemic *trans*-olefin **1** in hexane-CH_2Cl_2 (10:1), which concentration was approximately 0.02 mol/l, was carried out in a quartz cell with 180 Watt high pressure mercury lamp using 365 nm filter (band width = 10 nm, Ø = 5 cm) at 10°C for 12 hours. After evaporation of solvents under the reduced pressure, unstable *cis*-olefin **4** was obtained. The ratio between stable *trans*-olefin **1** (axial Me) and unstable *cis*-olefin **4** was determined by ^{1}H NMR to be 14:86. Unstable *cis*-olefin **4**; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.63-7.58 (4H, m), 7.45 (1H, br d, J = 8.4 Hz), 7.42 (1H, d, J = 8.4 Hz), 7.32-7.26 (2H, m), 7.19 (1H, d, J = 8.4 Hz), 7.16 (1H, br t, J = 7.7 Hz), 7.02 (1H, br t, J = 7.7 Hz), 6.31 (1H, dd, J = 8.4, 2.6 Hz), 5.94 (1H, d, J = 2.6 Hz), 3.51 (1H, dd, J = 10.1, 7.3 Hz), 3.33 (1H, dd, J = 12.4, 10.1 Hz), 2.99 (3H, s), 2.76 (1H, ddq, J = 12.4, 7.3, 7.0 Hz), 1.10 (3H, d, J = 7.0 Hz). Irradiation of solution of racemic *cis*-olefin **2** in hexane-CH_2Cl_2 (10:1), which concentration was approximately 0.02 mol/l, was carried out in a quartz cell with 180 Watt high pressure mercury lamp using 365 nm filter (band width = 10 nm, Ø = 5 cm) at 10°C for 12 hours. After evaporation of solvents under the reduced pressure, unstable *trans*-olefin **3** was obtained. The ratio between stable *cis*-olefin **2** (axial Me) and unstable *trans*-olefin **3** was determined by ^{1}H NMR to be 11:89. Unstable *trans*-olefin **3**; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.60 (1H, d, J = 8.7 Hz), 7.57 (1H, d, J =8.2 Hz), 7.50 (1H, d, J = 8.7 Hz), 7.44 (1H, d, J = 8.7 Hz), 7.41 (1H, d, J = 8.7 Hz), 7.31 (1H, d, J = 7.7 Hz), 7.19 (1H, d, J = 2.6 Hz), 7.13 (1H, br t, J = 7.7 Hz), 6.99 (1H, br t, J = 7.7 Hz), 6.85 (1H, dd, J = 8.7, 2.6 Hz), 6.71 (1H, ddd, J = 7.7, 6.9, 1.1 Hz), 6.42-6.36 (2H, m), 3.85 (3H, s), 3.52 (1H, dd, J = 9.9, 7.3 Hz), 3.32 (1H, dd, J = 12.1, 9.9 Hz), 2.74 (1H, ddq, J = 12.1, 7.3, 7.0 Hz), 1.17 (3H, d, J = 7.0 Hz). After irradiation of solution of racemic *cis*-olefin **2** in hexane, the solution was evaporated to concentrate to half

of its original volume under the reduced pressure and the concentrated solution was subsequently cool down to 5°C in the refrigerator to yield colorless block-shaped crystals of unstable *trans*-olefin **3** suitable for X-ray diffraction. A single crystal (dimensions of 0.50 x 0.50 x 0.40 mm) was selected for data collection and mounted on an Enraf-Nonius *CAD-4F*[1] diffractometer, interfaced to a *Debian-Linux* computer (Mo tube, 50 kV, 40 mA, monochromated Mo-K radiation (0.71073Å), $\Delta\omega = 1.15 + 0.34$ tg θ). Unit cell parameters and orientation matrix were determined from a least-squares treatment of the *SET4* setting angles of 22 reflections in the range $17.90° < \theta < 20.10°$. The crystal data of (2'*R**)-(*P**)-*trans*-olefin **3**: $C_{28}H_{22}OS_2$, *Mr* = 438.61; monoclinic; space group $P2_1/c$; a = 14.570(1), b = 7.376(1), c = 20.858(1)Å; β = 100.904(5)°; V = 2201.1(4)Å^3; Z = 4; Dx = 1.324 g cm^{-3}. The intensities of three standard reflections, monitored every three hours of X-ray exposure time, showed no greater fluctuations during data collection than those expected from Poisson statistics. The structure was solved by Patterson methods and extension of the model was accomplished by direct methods applied to difference structure factors using the program *DIRDIF*. The positional and anisotropic displacement parameters for the non-hydrogen atoms were refined. A subsequent difference Fourier synthesis resulted in the location of all hydrogen atoms, which coordinates and isotropic displacement parameters were refined. Final refinement on F^2 carried out by full-matrix least-squares techniques converged at $wR(F^2)$ = 0.1311 for 4783 reflections and $R(F)$ = 0.0440 for 3946 reflections with $F_o \geq 4.0\ \sigma(F_o)$ and 368 parameters. The final difference Fourier map was essential featureless: no significant peaks (0.32(6) e/Å^3) having chemical meaning above the general background were observed.

Irradiation of solution of racemic olefins **5** and **7** in toluene-d_8 was carried out in a NMR tube with 180 Watt high pressure mercury lamp using a Pyrex filter at room temperature. The concentration of solutions was approximately 0.1 mol/l, and irradiation was performed for 3

hours to reach the photostationary state, respectively. The ratio between stable **5** (axial Me) and unstable form **6** (equatorial Me) in the photostationary state was 8:92 and the ratio between stable **7** (axial Me) and unstable form **8** (equatorial Me) was 13:87 as determined by ^{1}H NMR. The samples were directly analyzed by ^{1}H NMR and used for thermodynamic studies to determine the flipping barrier. Stable form **5**; ^{1}H NMR (300 MHz, toluene-d_8) δ 7.86 (1H, d, J = 8.4 Hz), 7.43-7.40 (2H, m), 7.35-7.30 (3H, m), 7.16 (1H, d, J = 7.3 Hz), 7.08-6.88 (4H, m), 6.58 (1H, dd, J = 7.7, 1.1 Hz), 6.42 (1H, dt, J = 1.1, 7.7 Hz), 6.17 (1H, dt, J = 0.7, 7.7 Hz), 3.98 (1H, ddq, J = 7.3, 3.3, 6.6 Hz), 3.31 (1H, dd, J = 11.4, 7.3 Hz), 2.65 (1H, dd, J = 11.4, 3.3 Hz), 0.53 (3H, d, J = 6.6 Hz), unstable form **6**; ^{1}H NMR (300 MHz, toluene-d_8) δ 7.71-7.68 (1H, m), 7.43-7.34 (5H, m), 7.19 (1H, br d, J = 7.7 Hz), 7.00-6.87 (4H, m), 6.55 (1H, br d, J = 8.4 Hz), 6.39 (1H, dt, J = 1.1, 7.7 Hz), 6.16 (1H, dt, J = 1.1, 7.7 Hz), 3.02 (1H, dd, J = 9.9, 7.7 Hz), 2.92 (1H, dd, J = 12.1, 9.9 Hz), 2.28 (1H, ddq, J = 12.1, 7.7, 7.0 Hz), 0.84 (3H, d, J = 7.0 Hz), stable form **7**; ^{1}H NMR (300 MHz, toluene-d_8) δ 7.91 (1H, d, J = 8.4 Hz), 7.37 (1H, d, J = 8.4 Hz), 7.31-7.28 (3H, m), 7.20 (1H, d, J = 2.6 Hz), 7.07-6.89 (3H, m), 6.55 (1H, dd, J = 8.8, 2.6 Hz), 6.23 (1H, dd, J = 8.4, 2.6 Hz), 6.17 (1H, d, J = 2.6 Hz), 4.12 (1H, ddq, J = 7.0, 2.9, 6.6 Hz), 3.35 (3H, s), 3.34 (1H, dd, J = 11.4, 7.0 Hz), 2.76 (3H, s), 2.63 (1H, dd, J = 11.4, 2.9 Hz), 0.58 (3H, d, J = 6.6 Hz), unstable form **8**; ^{1}H NMR (300 MHz, toluene-d_8) δ 7.77 (1H, d, J = 8.1 Hz), 7.39-7.30 (3H, m), 7.17 (1H, d, J = 2.6 Hz), 7.12 (1H, d, J = 8.4 Hz), 7.07-6.91 (3H, m), 6.51 (1H, dd, J = 8.4, 2.6 Hz), 6.21 (1H, dd, J = 8.4, 2.9 Hz), 6.15 (1H, d, J = 2.9 Hz), 3.31 (3H, s), 3.07-2.96 (2H, m), 2.73 (3H, s), 2.40-2.26 (1H, m), 0.98 (3H, d, J = 6.6 Hz).

Irradiation of solution of racemic olefin **9** in benzene-d_8 was carried out in a NMR tube with 180 Watt high pressure mercury lamp using 365 nm filter (band width = 10 nm, Ø = 5 cm) at room temperature. The concentration of solution was approximately 0.05 mol/l, and

irradiation was performed for 24 hours to reach the photostationary state. The ratio between stable olefin **9** (axial Me) and unstable olefin **10** was determined by ^{1}H NMR to be 23:77. The sample was directly analyzed by ^{1}H NMR and used for thermodynamic studies to determine the flipping barrier. Stable form **9**; ^{1}H NMR (300 MHz, benzene-d_6) δ 7.58-7.55 (1H, m), 7.41-7.34 (4H, m), 7.29 (1H, dd, J = 8.1, 1.1 Hz), 7.08 (1H, dd, J = 8.1, 0.7 Hz), 7.05 (1H, m), 6.98 (1H, dd, J = 7.7, 1.5 Hz), 6.95-6.87 (2H, m), 6.55 (1H, ddd, J = 8.8, 7.3, 1.5 Hz), 6.52 (1H, dd, J = 7.7, 1.1 Hz), 6.05 (1H, ddd, J = 8.1, 7.3, 1.1 Hz), 4.08 (1H, ddq, J = 7.0, 2.2, 6.6 Hz), 3.36 (1H, dd, J = 11.0, 7.0 Hz), 2.72 (1H, dd, J = 11.0, 2.2 Hz), 0.53 (3H, d, J = 6.6 Hz), unstable form **10**; ^{1}H NMR (300 MHz, benzene-d_6) δ 7.51-7.46 (2H, m), 7.43-7.27 (3H, m), 7.23 (1H, dd, J = 8.1, 1.1 Hz), 7.10-6.82 (5H, m), 6.53 (1H, ddd, J = 8.8, 7.3, 1.5 Hz), 6.43 (1H, dd, J = 7.7, 1.5 Hz), 6.03 (1H, ddd, J = 8.8, 7.7, 1.1 Hz), 2.98 (1H, dd, J = 11.0, 9.9 Hz), 2.95 (1H, dd, J = 9.9, 7.0 Hz), 2.39 (1H, ddq, J = 11.0, 7.0, 7.0 Hz), 1.02 (3H, d, J = 7.0 Hz).